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(54) Glass/metal laminates

(57) A glass/metal laminate is provided which is characterised in that a glass ply 2 is bonded either directly or indirectly to a metal ply 1 by means of one or more synthetic resin or synthetic polymer layers 3 e.g. a layer of a polymer selected from epoxy resins or a copolymer containing ethylene and acrylic acid units, the glass ply being if desired coated by a light-reflecting coating to form a mirror.

FIG.1

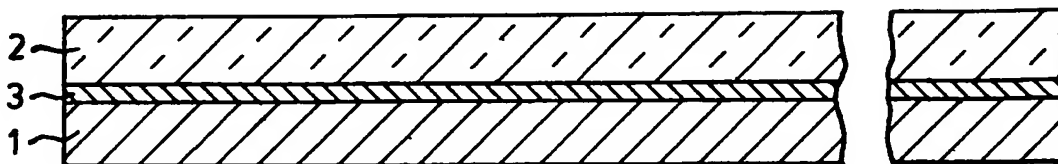


FIG.1

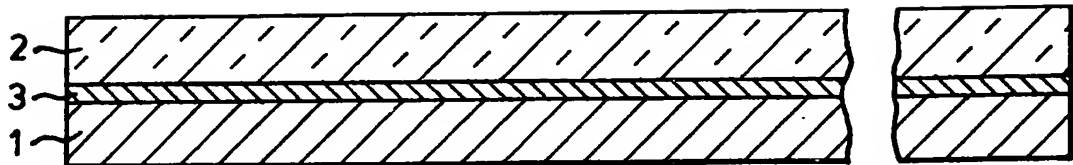
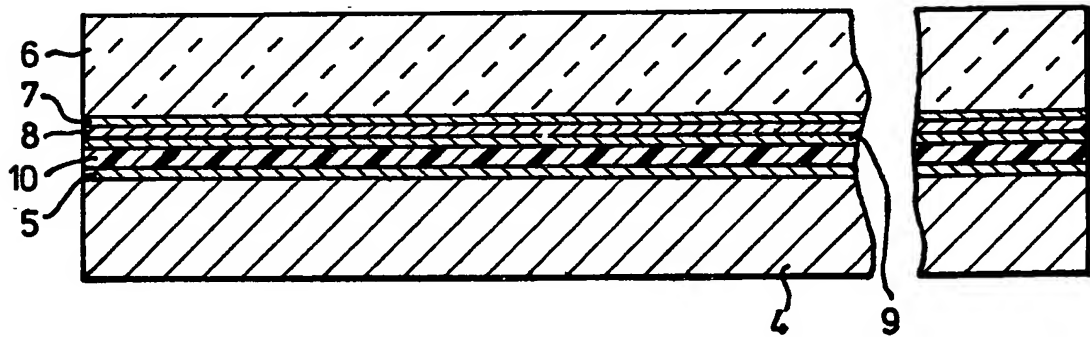


FIG.2



SPECIFICATION

Glass/metal laminates

- 5 This invention relates to glass/metal laminates. There are various potential fields of use for glass/metal laminates. Examples are the production of decorative panels, and the production of mirrors by bonding a glass ply, bearing a light-reflecting coating, to a metal backing-ply.

- 10 A problem encountered in practice is the production of a satisfactory bond between the glass and metal plies.

- According to the present invention there is provided a glass/metal laminate characterised in that the glass and metal plies are bonded together by means of one or more synthetic resin or synthetic polymer layers. By way of explanation, this definition includes laminates wherein the said plies are bonded together directly by said synthetic resin or polymer layer(s), and laminates wherein one or more layers additional to such bonding layer(s) is or are present between the said plies. For example the inner face of either or both said plies may bear a surface coating.

- Within the scope of the invention, laminates of various properties can be produced. These properties, for example the strength of the inter-ply bond and/or its durability, depend very much on the selection of the bonding medium. Particularly advantageous properties can be achieved by using a bonding medium comprising one or more resins and/or one or more synthetic plastics selected from categories hereinafter specified. However other factors also have an important influence on the properties of the laminate, for example the composition of the metal ply itself, the particular metal/bonding medium combination selected for the given product and the nature of the conditioning and/or pre-coating treatment (if any) to which the metal ply is subjected prior to the lamination step.

- Taking first the metal ply: this is preferably steel. Steel is recommended partly because of the very good mechanical properties which it can confer on the laminate. It enables appreciable strength to be obtained in relation to the thickness of the metal ply and it is compatible with the production of laminates which have a certain flexibility. In combination with these advantages, the use of a steel ply is particularly conducive to the attainment of strong and durable bonds by means of a bonding medium selected from resins and other synthetic polymers in accordance with the invention. Alternative metals which can be used for the metal ply include aluminium, stainless steel and brass.

- Preferably the metal ply is a galvanised steel ply. Such a ply has been found particularly beneficial because the corrosion-resistance of the ply improves the durability of the laminate in various environments of use. Moreover the galvanising treatment so conditions the steel that stronger metal/glass bonds can often be achieved, or bonds of a given strength

can be achieved more easily.

- 65 The metal ply is preferably steel which has been galvanised and bonderised.

- As an alternative to galvanising and/or borderising (or in addition to either or both such treatments if appropriate) the metal ply can be provided with a protective coating of another kind, on one or more faces, for example a protective plastics coating and/or a coating of a priming composition.

- The invention includes, as particularly advantageous embodiments, glass/metal laminates characterised in that the metal ply has a primed face which is bonded to the glass ply by means of one or more synthetic resin or synthetic polymer layers.

- Very suitable primers are to be found in each of the categories: epoxy resins, including epoxy ester resins, vinyl polymers e.g. polyvinylchloride and polyvinylidene fluoride, melamine and melamine-formaldehyde resins, acrylic resins, short and long chain polyesters, alkyd-melamine resins, phenolic resins, polyurethane resins, ethylene/vinyl acetate, ethylene/acrylic acid and ethylene/vinyl acetate/acrylic acid copolymers. Certain of such primers e.g. acrylic resins and polyester resins, can usefully be mixed with a certain amount of a silicone resin, which improves adhesion to certain bonding media.

- The metal ply can advantageously be primed with two or more priming coats which may be of the same or different compositions.

- The efficacy of any given type of primer is dependent in some measure on the particular bonding layer composition selected in a given case. However certain of such primers are effective with a variety of different bonding media. Preferred groups of primers are (A) ethylene/acrylic acid, ethylene/vinylacetate and ethylene/vinyl acetate/acrylic acid copolymers, and (B) epoxy resins. Such primers can be applied e.g. as an emulsion or solution.

- Accordingly the invention includes, as particularly important embodiments thereof, a glass/metal laminate characterised in that the metal ply, e.g. a steel ply, on at least that face thereof which is internal of the laminate bears at least one primer selected from said groups (A) and (B) and in that the primed metal ply and the glass ply are bonded together by one or more synthetic resin or synthetic polymer layers. In certain very advantageous embodiments use is made of a said metal ply, primed with one or more of such primers and a bonding medium which is also based on one or more polymers of the same class.

- Referring now to the bonding layer(s): use can be made for example of one or more film-forming polymers which may be applied in sheet, e.g. thin foil, form and caused to adhere to the laminate plies by subjecting the assembly to heat and pressure.

- A particularly preferred bonding medium is polyvinylbutyral. This material is convenient to use and enables very strong metal/glass bonds to be achieved which are durable under a useful range of temperature and other fluctuating environmental conditions.

One particularly recommended product according

to the invention incorporates a metal ply (preferably a steel ply, e.g. a bonderised steel ply) having at least its internal face primed with one or more epoxy resins, and between such primed face and the glass ply, a bonding layer of polyvinylbutyral.

- 5 Other bonding media which have been found to give very good results are in the class of epoxy resins. When employing epoxy resins it is beneficial to employ a mixture of epoxy resins of different
10 molecular weights to achieve a favourable combination of high bond strength with sufficient elasticity of the bonding layer to allow for slight relative parallel displacement of the bonded faces of the metal and glass plies, for example in consequence of flexure of
15 the laminate or differential thermal expansion of such plies. When using such a bonding medium it is very suitable to use a metal ply primed with an epoxy ester based primer.

- 20 Another recommended category of bonding media comprises polyurethane adhesives. When using such a bonding medium, it is very suitable to use a metal ply primed with a polyester based primer. As an alternative a primer based on a polyurethane resin or a melamine resin can be used.

- 25 Yet another recommended category of bonding media comprises hot-melt adhesives. Among laminates incorporating a bonding layer formed from a hot-melt type composition, the invention includes such laminates wherein the metal ply is a ply (e.g. a
30 steel ply) whose internal face has been primed with a primer based on one or more polymers of group (A) hereinbefore referred to.

- The employment of hot-melt type adhesives affords a number of advantages. Among these are
35 the facility with which they can be handled and applied to form bonding layers of predetermined thickness and uniformity. Reproducible results can be achieved under rapid assembly conditions. It is an easy matter to select a hot-melt adhesive formulation which will have a required combination of prop-
40 erties. The hot-melt adhesive composition can be selected to combine a very adequate bond strength with a high degree of impermeability by moisture. The use of a hot-melt type adhesive also contributes
45 to lowering of production costs. This is due to the relatively low cost of the adhesive itself and the ease with which bonding can be achieved with very modest equipment and in a small working area.

- The hot-melt adhesive is preferably one which is
50 molten at a temperature of 150°C or lower, preferably between 60° and 120°C.

- Hot-melt adhesive formulations include an elastomeric or thermoplastic material which melts easily to a low viscosity fluid. In order to achieve solidified
55 bonding layers of adequate strength and cohesiveness such easily meltable ingredient is blended with a higher molecular weight polymeric material. A very favourable balance of properties can be achieved by formulating the hot-melt adhesive to
60 incorporate a combination of resins of different melt indices.

- Examples of relatively easily meltable substances which can be used in hot-melt adhesive formulations are various natural and synthetic resins and waxes,
65 e.g. terpene resins, hydrocarbon resins polyter-

penes, phenolformaldehyde resins, alkyds, coumarone-indene resins, rosin and rosin derivatives and mineral, vegetable and petroleum waxes.

- In preferred embodiments of the present invention
70 a hot-melt adhesive composition is used which includes one or more tackifiers selected from terpene and phenolic resins and microcrystalline waxes. Very good results are also attainable with styrenes and low-molecular homologues.

- 75 The proportion of tackifier(s) in the composition influences the melt viscosity of the adhesive.

- Examples of higher molecular weight synthetic polymeric materials suitable as reinforcing or toughening ingredient of the hot melt adhesive
80 composition, forming what is sometimes referred to as the adhesive backbone, are polyvinyl acetate, polyethylene, polyisobutylene (butyl rubber), polystyrene and styrene copolymers, ethyl cellulose, polyamides derived from dimerized fatty acids and
85 diamines, and butyl methacrylates.

In preferred embodiments of the present invention a hot-melt adhesive is used which includes one or more elastomers or thermoplastics selected from butyl rubber and ethylene/vinyl acetate copolymers.

- 90 The hot-melt adhesive may incorporate various other types of ingredients for conferring required properties. Examples of categories in which such supplementary ingredients fall are plasticisers, thermal stabilizers and fillers.

- 95 As plasticizers, use can be made of various resins which serve to improve adhesive wetting of the surfaces to be bonded, and the flexibility of the adhesive layers. Examples of plasticizers are phthalates, phosphates, chlorinated polyphenyls, rosin derivatives and polyesters.
100

Stabilizers are used in hot-melt adhesives to improve the thermal stability of the composition. The stabilizers most usually employed are anti-oxidizing agents, e.g., steric phenols and phosphite derivatives.
105

Fillers are used for modifying the physical properties of the adhesive compositions. They are substantially chemically inert under their conditions of use. Suitable fillers are e.g. zinc oxide, calcium carbonate,
110 titanium dioxide, barium sulphate and carbon black. Generally, it is preferable to employ inorganic fillers. These may have the effect of reducing the weight of the adhesive or colouring it or of reducing the viscosity or mechanically strengthening the product. However organic fillers such as resins may also be used.
115

Advantageously the hot-melt adhesive incorporates one or more saturated hydrocarbons. The presence of such hydrocarbon(s) increases the resistance of the adhesive to penetration by water.

- 120 Examples of suitable saturated hydrocarbons are paraffin, chlorinated paraffins, polybutenes and polyisobutylenes.

- It will be apparent that a particular given ingredient of the hot-melt adhesive can fulfil different important functions in the product. For example a saturated hydrocarbon can be selected to serve as an ingredient of the adhesive backbone, to contribute to surface-tack, and to have plasticizing and stabilising functions. As another example, a tackifier
125 may be selected which also confers excellent water-
130

resisting properties on the adhesive. Waxes, e.g. fatty-acid ester/alcohol mixtures, are very effective tackifiers and also have good water-resisting properties. In addition they can be used to influence the viscosity of the hot-melt so as to obtain a low melting point.

Preferably the thickness of the or each layer of hot-melt adhesive (when used) is less than 150 microns. This condition is recommended because it exploits an important property of hot-melt adhesives, namely their ability to give very effective bonds, even as very thin layers, and because such thin layers leave a very small surface area of adhesive exposed to the environmental atmosphere.

In preferred embodiments, a hot-melt adhesive is used the water resistance of which is less than 0.5 and most preferably less than 0.1 g H₂O per m² of surface per 24 hrs per mm thickness per cm Hg of pressure.

The invention also includes laminates as hereinbefore defined wherein the glass and metal plies are bonded by means of an acrylic resin based adhesive.

The invention further includes laminates as hereinbefore defined wherein the glass and metal plies are bonded by means of a polyvinylchloride bonding layer. In this case it is very suitable to employ an epoxy or a phenolic resin primer or a melamine resin primer on the metal ply.

In some embodiments of the invention, the metal and glass plies are bonded together by means of two or more different bonding media. For example the invention includes laminates in which said plies are bonded together by means of two or more bonding layers of different compositions. In certain products in this category the said plies are bonded together by means of an adhesively coated thermoplastics foil, applied as such between the glass and metal plies prior to application of laminating conditions, normally heat and pressure. A specific example giving very good results employs for the bonding function a foil of a polyester bearing a coating of an acrylic resin based adhesive on each side thereof. Such double-coated foils are commercially available. Suitable such foils are for example those marketed under the trade marks MACBOND 2800 and MACBOND 2132.

The bonding layer(s) of a laminate according to the invention can incorporate reinforcement, e.g. a fibrous or filamental reinforcement composed of glass or polyamide fibres or filaments. The reinforcement can be resin-impregnated.

The actual bonding step in the manufacture of the laminate may be achieved by means of calender rolls or by means of a press. In order to avoid occlusions of air or other gases between the plies, bonding under heat and pressure can be achieved within a chamber in which the assembly of plies and bonding medium or bonding media is subjected to a predetermined schedule of heat and pressure variations. The margins of the assembly may be placed in communication with a suction device which suction forces are propagated to the inter-ply zone(s) to promote evacuation of gases therefrom. The exertion of such suction force can be controlled in timed relation to the incidence of predetermined ambient

heat and/or pressure conditions in the course of a heating and pressing cycle within a said chamber. Such bonding techniques are known per se in relation to the manufacture of other kinds of laminates, in particular glass/glass laminates (see e.g. United Kingdom Patent No 1,368,785).

The glass ply of a laminate according to the invention can be tempered. For example the glass ply may be a sheet of chemically tempered glass.

The invention is applicable with special benefits in the production of mirrors or other radiant-energy reflectors in which a ply, e.g. the glass ply, bears a radiation-reflecting coating or coatings. In such reflector production, the radiation-reflecting coating(s) can be formed on the external face of the glass ply, either before or after lamination thereof to the metal ply, or such coating(s) can be formed prior to lamination on the internal face of the glass ply. Preferably said coating(s) is or are formed on said internal face. For example such internal face can bear a silver layer, deposited by one of the well-known methods, and one or more protective coatings on such silver layer. For example the silver layer may be successively covered by a layer of copper and a layer of protective paint, which layers may likewise be formed in well-known manner. A metal other than silver can be used, e.g. aluminium or copper.

As an alternative to the use of a reflecting coating on the glass, a reflector according to the invention can comprise a metal ply which provides a radiant energy reflecting inner face, this face being covered by the glass ply.

The invention is very useful for producing mirrors for use as or as part of a solar energy reflector. In such products it is necessary for the glass/metal bond to be adequate to endure strains imposed under the heating effects to which the laminate is exposed in use and it is often necessary for the bond to remain fully effective notwithstanding exposure to all normal variations in atmospheric conditions. Bonds of the requisite standards can be achieved by carrying out the present invention in its preferred embodiments as herein referred to.

Provided the moduli of elasticity of the glass and metal plies and the efficiency of the inter-ply bond are appropriate, a flat laminate according to the invention can be appreciably flexed in a direction which imparts a concave curvature to the front face of the glass ply. During such flexure, the metal ply and the bond between the glass and metal plies reduces the tensile loading of the rear, i.e. the internal face of the glass ply and may in fact prevent that rear face from being subjected to any tensile stress. The imposition of tensile surface stresses in the glass can of course lead to breakage, particularly if there are surface flaws in the glass which act as stress raisers. By appropriate choice of the said ply thickness and elasticity moduli parameters, and by creating an efficient inter-ply bond in accordance with the invention, a laminate can be produced which can be flexed as referred to without breaking the glass, even when using a piece of untempered glass and one which has not been specially surface-treated to remove surface flaws. Following flexure of the laminate it can be installed in a holding device

which holds the laminate in curved condition, against elastic recovery forces in the laminate.

5 Preferably the relative thicknesses of the glass and metal plies, their elasticity moduli and the efficiency of the inter-ply bond are such that the rear face of the glass ply is not subjected to tensile stresses by the flexing of the laminate to confer on the front face of the glass ply a radius of curvature of 10 metres, and most preferably such that radius can be reduced to 1
10 metre without said rear face being subjected to tensile stress. And most preferably said thickness, moduli and bond efficiency are such that by flexing the laminate to a radius of 10 metres (and preferably even when reducing the radius to 1 metre) said rear
15 face as well as the front face of the glass ply is subjected to compressive stresses.

The relative thicknesses of the glass and metal plies must be suitable having regard to the elasticity moduli of the glass and metal, the efficiency of the inter-ply bond and the radius or radii of curvature to which the laminate is to be fixed. Other things being equal, the higher the elasticity modulus of the metal is in relation to that of the glass, the lower can be the thickness ratio t_m/t_g , wherein t_m is the thickness of the metal and t_g the thickness of the glass. By
20 the efficiency of the inter-ply bond is meant the efficiency with which it can transmit stresses from the metal to the glass when the laminate is flexed. An ideal bond of 100% efficiency would be one which resulted in the laminate behaving as a monolithic structure in regard to the stress distribution profile through its thickness. In practice, for ensuring that the rear face of the glass is subjected only to compressive stresses the laminate should satisfy the condition $t_m E_m > t_g E_g$, where t_m and t_g are the thicknesses of the metal and glass, as above stated, and E_m and E_g are their elasticity moduli, the difference in magnitude between the two values $t_m E_m$ and $t_g E_g$ being sufficient, having regard to the extent to which
25 the laminate is flexed, to allow for the imperfect efficiency of the bond. Preferably $t_m E_m \geq 1.1 \times t_g E_g$.

It is particularly advantageous to select the thicknesses of the metal and glass plies so that the laminate is between 1.0 and 4.0 mm in thickness. Within
30 this range curved mirrors which are very satisfactory, for example for solar energy reflection purposes, can be made at low or moderate cost.

Preferably the glass ply has a thickness between 0.6 and 1.0 mm. Such plies can be very easily bent.
35 Glass below about 0.6 mm in thickness tends to be too liable to breakage before or during bonding to the metal ply. Glass plies in the said thickness range are very suitable in solar energy reflectors because the glass absorbs very little solar energy.

Preferably the metal ply has a thickness less than 3.0 mm and most preferably from 0.3 to 2.5 mm. Such metal plies are preferred because of the ease with which they can be flexed. When using a metal ply of ordinary steel, the most preferred thickness range for the ply is from 0.4 to 1.0 mm.
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It is within the scope of the invention for the laminate to incorporate plies additional to the bonded metal and glass plies. For example the front face of the glass ply, i.e. its face remote from said metal ply,
45 can bear a protective film. The metal ply which is

bonded to the glass ply can also be bonded to another ply, e.g. a sheet of plastics.

The inter-ply bond in a laminate according to the invention is preferably such that the laminate is highly resistant to the ingress of moisture between the plies. The penetration of water, e.g. atmospheric moisture, between the plies may have harmful effects on the structure and/or the physical or chemical properties of laminate materials and particularly
50 of any optical coating which may be present as for example in the case of a mirror.

Certain embodiments of the invention, selected by way of example, will now be described with reference to the accompanying drawings comprising
55 Figures 1 and 2 which are cross-sectional views of two different laminates according to the invention.

The laminate illustrated in Figure 1 comprises a metal ply 1 and a glass ply 2, bonded together by means of a bonding layer 3.

By way of example, ply 1 is a galvanised steel ply which prior to lamination with the glass ply has been primed, at least on its face which is to be bonded to the glass ply, with a priming composition based on an ethylene/vinyl acetate/acrylic acid copolymer applied as an emulsion. The primed galvanised steel ply is bonded to the glass ply 2, which is an untempered sheet of ordinary soda lime glass, by means of a bonding layer 3 formed of a film of hot-melt based on ethylene/vinyl acetate polymer. Bonding is
60 achieved by subjecting the metal and glass plies and intervening hot-melt film to heat and pressure to cause softening of the polymer layer and intimate pressure contact between the softened polymer and the glass and metal plies. An extremely strong inter-ply bond is achieved.
65

Other laminates according to the invention, having similarly good properties were produced using the same method except that in one case an ethylene/acrylic acid copolymer and in another case an ethylene/vinyl acetate copolymer was used as the priming agent instead of the terpolymer.

Yet other laminates according to the invention comprised a galvanised steel ply which had been bonderised and primed with a layer of epoxy resin 5 microns thick and with a superimposed coating of melamine formaldehyde resin 20 microns thick. The bonderised and primed steel ply was bonded to a sheet of glass by means of a polyvinylbutyral film or foil using a calendering procedure or by subjecting the assembly to heat and pressure in a chamber, preferably with the exertion of suction forces at the margin of the assembly, as hereinbefore referred to.
70

Another very satisfactory laminate according to the invention was formed by a mirror bonded to a galvanised steel ply using a layer of an epoxy resin composition for the bonding layer. This composition comprised, in parts by weight: 50 part Epon 815 (epoxy resin marketed by Shell Chemical Company),
75 40 parts of epoxy resin D732 (marketed by Dow Corning Corp.), 55 parts of Versamid 140 (polyamide resin marketed by General Mills), and 10 parts of TBN (amino-terminated butadiene).

In another embodiment the same assembly was used except that the metal ply was furnished with a
80

primer based on an epoxy ester. In this case a product was obtained which was of better quality having improved resistance to ageing.

- In a further embodiment the mixture of epoxy resins was replaced by a single epoxy resin, e.g. Araldite AY103 (marketed by Ciba Products Company). The resulting laminate was very satisfactory. The ageing resistance of such a laminate could likewise be improved by providing the metal ply with a coating of an epoxy ester.

The laminate shown in Figure 2 comprises a galvanised steel ply 4 bearing a primer coating 5, and a glass ply 6 which on its inner face bears a silver coating 7, covered by protective coatings 8, 9 of copper and paint as known per se in mirror production. The glass ply is an untempered sheet of ordinary soda-lime glass, 0.8 mm in thickness. The metal ply also has a thickness of 0.8 mm.

The priming of the galvanised steel ply prior to lamination was effected by applying an epoxy resin layer of about 5 microns in thickness and then a second priming layer of 20 microns in thickness using an epoxy ester primer.

Bonding was achieved using a polyvinyl butyral foil 10 having a thickness of 0.76 mm. The assembled plies with the intervening bonding medium were subjected to heat and pressure. Following the bonding operation the laminate could be flexed to impart to the exposed face of the glass ply a concave curvature. Similar results can be obtained by using a polyester film carrying on each face an acrylic resin based adhesive, for bonding the steel ply to the silvered and protectively coated glass ply.

CLAIMS

1. A glass/metal laminate characterised in that the glass and metal plies are bonded together by means of one or more synthetic resin or synthetic polymer layers.
2. A laminate according to claim 1, characterised in that said metal ply is a steel ply.
3. A laminate according to claim 2, characterised in that said metal ply is a galvanised steel ply.
4. A laminate according to claim 2, characterised in that said metal ply is a galvanised and bonderised steel ply.
5. A laminate according to any preceding claim, characterised in that said metal ply bears a protective plastics coating.
6. A laminate according to any preceding claim, characterised in that that face of said metal ply which is bonded to the glass ply bears a priming coating of one or more synthetic resin or synthetic polymer layers.
7. A laminate according to claim 6, characterised in that the priming coating incorporates an epoxy resin or an epoxy ester resin.
8. A laminate according to claim 6, characterised in that the priming coating incorporates an ethylene/vinyl acetate, ethylene/acrylic acid or ethylene/vinyl acetate/acrylic acid or a mixture of two or more such copolymers.
9. A laminate according to claim 6, characterised in that the priming coating incorporates one or more primers belonging to one or more to the categories: vinyl polymers e.g. polyvinylchloride or

polyvinylidene fluoride, melamine and melamine-formaldehyde resins, acrylic resins, short and long chain polyesters, alkyd-melamine resins, phenolic resins and polyurethane resins.

10. A laminate according to any of claims 6 to 9, characterised in that said priming coating also incorporates a quantity of a silicone resin.

11. A laminate according to any of claims 6 to 10, characterised in that the compositions of the priming coating and the bonding layer(s) are based on one or more polymers of the same group.

12. A laminate according to any of claims 1 to 11, characterised in that there is a said bonding layer which has been formed from one or more film-forming polymers applied in sheet form.

13. A laminate according to claim 12, characterised in that there is a said bonding layer of polyvinylbutyral.

14. A laminate according to claim 13, characterised in that that face of said metal ply which is bonded to the glass ply bears a priming coating of one or more epoxy resins.

15. A laminate according to any of claims 1 to 14, characterised in that there is a said bonding layer comprising an epoxy resin bonding medium.

16. A laminate according to claim 15, characterised in that said bonding medium comprises a mixture of epoxy resins of different molecular weights.

17. A laminate according to claim 15 or 16, characterised in that that face of said metal ply which is bonded to the glass ply bears a coating of an epoxy ester based primer.

18. A laminate according to any of claims 1 to 17, characterised in that there is a said bonding layer which comprises a polyurethane adhesive bonding medium.

19. A laminate according to claim 18, characterised in that the face of said metal ply which is bonded to the glass ply bears a coating of a polyester based primer, or a primer based on a polyurethane or a melamine resin.

20. A laminate according to any of claims 1 to 19, characterised in that there is a said bonding layer which comprises a hot-melt adhesive bonding medium.

21. A laminate according to claim 20, characterised in that the face of said metal ply which is bonded to the glass ply bears a priming coating comprising an ethylene/acrylic acid, ethylene/vinylacetate or ethylene/vinyl acetate/acrylic acid copolymer or a mixture of two or more such copolymers.

22. A laminate according to claim 20 or 21, characterised in that the hot-melt adhesive is one which is molten at a temperature of 150°C or lower, preferably between 60° and 120°C.

23. A laminate according to any of claims 20 to 22, characterised in that said hot-melt adhesive bonding medium comprises one or more elastomers or thermoplastics selected from butyl rubber and ethylene/vinyl acetate copolymers.

24. A laminate according to any of claims 20 to 23, characterised in that said hot-melt adhesive bonding medium incorporates one or more saturated hydrocarbons.

25. A laminate according to any of claims 20 to 24, characterised in that the said bonding layer is less than 150 microns in thickness.

5 26. A laminate according to any of claims 1 to 25, characterised in that there is a said bonding layer which comprises an acrylic resin based adhesive.

27. A laminate according to any of claims 1 to 26, characterised in that there is a said bonding layer which comprises a polyvinylchloride bonding
10 medium.

28. A laminate according to claim 27, characterised in that the face of said metal ply which is bonded to the glass ply bears a coating of an epoxy or a phenolic or a melamine resin primer.

15 29. A laminate according to any of claims 1 to 28, characterised in that said glass and metal have been bonded together by means of an adhesively coated thermoplastics foil.

30. A laminate according to any preceding claim
20 characterised in that the glass ply bears (a) radiation-reflecting coating(s).

31. A laminate according to claim 30, characterised in that said radiation-reflecting coating(s) is or are on that side of such ply which faces the metal
25 ply.